crystal specimens. These values have been used to predict the Hall coefficient for polycrystalline samples, and the possibility of using polycrystalline specimens to determine the independent coefficients has been investigated. It is concluded that good quantitative values will only be obtained if it is possible to obtain specimens with very different textures.

Spin-Lattice Relaxation in Free-Radical Complexes

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Spin-spin and spin-lattice relaxation times have been determined at 19.3 Mc/sec for samples of 1,1-diphenyl-2-picrylhydrazyl, picryl-N-aminocarbazyl, and their recrystallized samples from various solvents. It is found that the spin-lattice relaxation time increases in most of the recrystallized samples and the melting points of the samples decrease. It has been possible to explain these results in terms of variable exchange interaction due to a possible change in lattice. The three-reservoir model of Bloembergen and Wang has been used in order to evaluate the relaxation times for spin to exchange and exchange to lattice.

INTRODUCTION

IN solids, spin-lattice relaxation time gives valuable information regarding the structure of the lattice and spin-orbit coupling. Though in free radicals, the spin-orbit coupling is weak and spin-lattice relaxation time is usually large, yet it has been found possible to determine it by measuring the linewidth for two values of the radio-frequency fields.

We have determined T_1 and T_2 the spin-lattice and spin-spin relaxation times for 1,1-diphenyl-2-picrylhydrazyl, picryl-N-aminocarbazyl, and their recrystallized samples from various solvents. The melting points of the samples have also been determined for all the

cases. It is found that increase in spin-lattice relaxation time is accompanied by a decrease in melting point. A large change in spin-lattice relaxation time is not necessarily accompanied by a large change in linewidth. It has been possible to explain these results in terms of possible change in lattice. The three-reservoir model of Bloembergen and Wang[1] has been used in order to evaluate the relaxation times from spin to exchange and exchange to lattice.

EXPERIMENTAL TECHNIQUE

An rf electron spin-resonance spectrometer at 19.3 Mc/sec using a Clapp-type oscillator and detector, shown in Fig. 1, has been used here for this work. The sensitivity is sufficiently high when it is oscillating weakly, and the method is found to be most convenient for this measurement. The spin-spin relaxation time T_2 and spin-lattice relaxation time T_1 have been determined by measuring the half-linewidth between half-maximum points, and for two values of the rf magnetic fields H_1 and H_2, respectively. The expressions for the half-linewidth derived from the Bloch[2] equations are as follows:

$$\delta_1 = [1 + (\gamma H_1)^2 T_1 T_2]^{1/2}/\gamma T_2, \qquad (1)$$

$$\delta_2 = [1 + (\gamma H_2)^2 T_1 T_2]^{1/2}/\gamma T_2, \qquad (2)$$

where $\gamma = g\beta/\hbar$. The expressions for T_1 and T_2 can be written by squaring and rearranging the Eqs. (1)
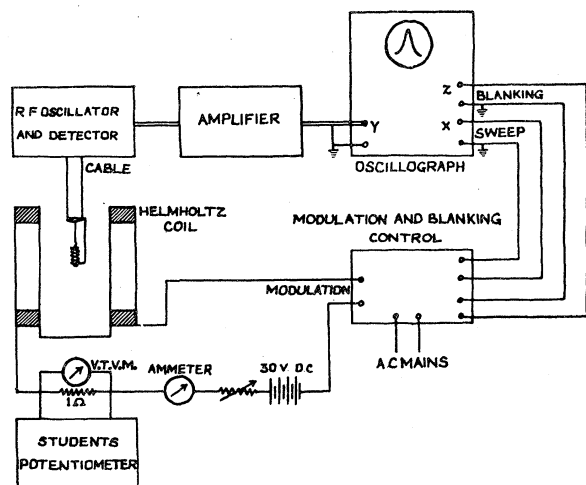

FIG. 1. Block diagram of electron spin resonance rf setup.

[1] N. Bloembergen and S. Wang, Phys. Rev. **93**, 72 (1954).
[2] F. Block, Phys. Rev. **70**, 460 (1946).

and (2):

$$T_1 = \Delta D^2 / [\gamma(\Delta H^2 \times \Delta P^2)^{1/2}], \qquad (3)$$

$$T_2 = \Delta H^2 / [\gamma(\Delta H^2 \times \Delta P^2)^{1/2}], \qquad (4)$$

where

$$\Delta D^2 = \delta_2^2 - \delta_1^2,$$

$$\Delta H^2 = H_2^2 - H_1^2,$$

and

$$\Delta P^2 = \delta_1^2 H_2^2 - \delta_2^2 H_1^2.$$

The value of the high-frequency field in the tank coil is given by

$$H_1 = (2\pi N K \sqrt{2}/10l) I_L, \qquad (5)$$

where N is the number of windings in the coil, l is the length of the coil, I_L is the current in the coil, and K is Nagoaka factor for short solenoid and in this case the value is 0.66. I_L can be determined by measuring the voltage E across the tank-coil line and knowing its impedance Z_t. The measurements of δ_1 and δ_2 have been made for two values of E corresponding to H_1 and H_2. The value of Z_t, the impedance of the line was calculated by the standard formula, and the value of E was measured by a vacuum-tube voltmeter.

EXPERIMENTAL RESULTS AND INTERPRETATIONS

The spin-spin and spin-lattice relaxation time have been determined at room temperature by measuring linewidth at two different rf voltages, 0.9 and 5.0 V and at 19.3 Mc/sec. The values of the relaxation times T_1 and T_2 have been computed with the help of the formulas (3) and (4).

The melting points of all the samples have also been measured. The experimental data of all the samples are given in Table I. It is observed that the values of the spin-lattice relaxation time T_1 has increased considerably in those recrystallized samples which show large change in their melting points. It seems that in these samples some change in the lattice has taken place. The spin-lattice relaxation time T_1 depends upon spin-orbit coupling constant λ, the energy difference

TABLE I. Relaxation time at room temperature (300°K) at 19.3 Mc/sec. T_1=spin-lattice relaxation time; T_2=spin-spin relaxation time.

Samples	$(\Delta H_{1/2})_1$ $E_1 = 0.9$ V $H_1 = 0.02$ Oe	$(\Delta H_{1/2})_2$ $E_2 = 5.0$ V $H_2 = 0.12$ Oe	$T_1 \times 10^8$ sec	$T_2 \times 10^8$ sec	mp °C
DPPH powder	1.78	1.80	7.70	6.39	137.0
DPPH recrystalized from:					
Benzene	1.80	1.89	23.80	6.38	125.0
Carbon tetrachloride	2.27	2.58	134.30	5.05	120.0
Chloroform	2.13	2.40	115.20	5.38	115.0
Carbon disulfide	3.34	3.61	113.60	3.42	105.0
Toluene	3.91	4.21	124.30	2.92	105.0
Nitrobenzene	2.45	2.88	185.80	4.67	105.0
Dioxane	2.37	2.88	197.90	4.83	100.0
Amylacetate	2.65	3.12	205.80	4.32	100.0
Xylene	2.32	2.90	258.90	4.95	75.0
PAC powder	0.62	0.68	25.10	18.10	215.0
PAC recrystalized from:					
Carbon tetrachloride	0.67	0.73	22.80	16.93	205.0
Carbon disulfide	0.73	0.79	23.50	15.56	200.0
Chloroform	0.85	0.90	21.46	13.41	210.0
Benzene	1.02	1.06	17.32	11.15	210.0

between two orbital levels Δ, and the temperature T in the following manner[3]:

$$T_1 \propto \Delta^M/\lambda^2 T^N, \qquad (6)$$

where M and N have numerical values depending upon the type of processes.

In free radicals the energy gap between the two orbital levels is very large and so the slight variations in Δ values will not effect the spin-lattice relaxation time appreciably. The change in spin-orbit coupling constant λ may occur due to the thermal vibrations of the lattice or the molecule as a whole may be coupled to the orbital motion of the electrons, and thus the spin-orbit coupling constant λ may change the spin-lattice relaxation time to a greater amount due to slight changes produced in the lattice. Apart from these interactions there are other mechanisms also which may be more effective in pumping the energy from the spin system to the lattice. The molecular motions are one of the most important factors in controlling the electron spin-resonance linewidth and relaxation times. Addition complexes are formed when these free radicals are recrystallized from different solvents on account of which slight changes in the lattice are produced. An attempt to confirm this view was made by taking x-ray powder photographs of these samples. Good photographs could not be obtained due perhaps to the fact that a large fraction of the substance is amorphous in nature and therefore this method of analysis could not be extended further. An analysis of the data on all the samples enables us to classify them in the following manner:

Class I: DPPH/xylene, DPPH/amylacetate, DPPH/dioxane, and DPPH/nitrobenzene, where the spin-lattice relaxation time has considerably increased and the melting point has been lowered but the linewidth has not increased much.

Class II: DPPH/toluene, DPPH/carbon disulfide, DPPH/chloroform, and DPPH/carbon tetrachloride, where the linewidth has increased more than class I samples but increase in T_1 and decrease in the melting point is less than class I samples.

Class III: DPPH/benzene and all the samples of picryl-N-amino carbazyl, where changes in linewidth, spin-lattice relaxation time, and melting point are very small.

In order to get a more complete picture from our experimental measurements, the three-reservoir model of Bloembergen and Wang has been used in computing the values of spin-exchange relaxation time T_{1a} and exchange-lattice relaxation time T_{1b}.

The model indicates that the excited spins can relax to the lattice through exchange or directly. In view of

[3] D. J. E. Ingram, *Free Radicals as Studied by Electron Spin Resonance* (Butterworths Scientific Publications, London, 1958), p. 126.

comparatively large exchange-energy reservoir, they further assume that the direct relaxation to the lattice is not possible and the effective relaxation process is from the spin system to the exchange and then to the lattice. In cases where strong exchange narrowed resonance lines are observed, the nonadiabatic part of the linewidth which depends upon the spin-lattice relaxation time or the transfer of energy from the Zeeman system to the lattice will depend upon the time which is taken in transferring the energy from the spin to the exchange system. The expression for the relaxation time which does not depend upon the lattice phonons is given by:

$$1/T_{1a} \approx (1/T_2) \exp(-\omega_Z{}^2/\omega_E), \qquad (7)$$

where ω_Z and ω_E are Zeeman and exchange frequencies. The relaxation time T_{1a} is independent of lattice temperature and the exchange-lattice relaxation time T_{1b} will depend upon lattice temperature θ_L. The expression for spin temperature θ_Z exchange temperature θ_E, lattice temperature θ_L and $(T_1)_{\text{eff}}$ have been given[4] as:

$$\theta_Z/\theta_L = [1 + \gamma^2 H_1{}^2 T_2 (T_1)_{\text{eff}}], \qquad (8)$$

$$\frac{\theta_E}{\theta_L} = \frac{[1 + \gamma^2 H_1{}^2 T_2 (T_1)_{\text{eff}}]}{[1 + \gamma^2 H_1{}^2 T_2 T_{1a}]}, \qquad (9)$$

$$\theta_Z/\theta_E = [1 + \gamma^2 H_1{}^2 T_2 T_{1a}], \qquad (10)$$

$$(T_1)_{\text{eff}} = [T_{1a} + (K_Z/K_E) T_{1b}], \qquad (11)$$

$$\left(\frac{K_Z}{K_E}\right) = \left[\frac{U_Z}{U_E} \cdot \frac{\theta_Z}{\theta_E}\right], \qquad (12)$$

where U_Z and U_E are the energies of the spin and exchange systems, respectively. With the help of Eq. (7), the relaxation time T_{1a} which is responsible for transferring the energy from the Zeeman system to the exchange system has been calculated. The values of ω_E

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[4] J. P. Goldsborough, M. Mandel, and G. E. Pake, Phys. Rev. Letters 4, 13 (1960).

TABLE II. T_{1a} and T_{1b} at room temperature at 19.3 Mc/sec.

Samples	T_{1a} sec	T_{1b} sec
DPPH powder	6.39×10^{-8}	4.54×10^{-5}
DPPH recrystalized from:		
Benzene	6.38×10^{-8}	4.71×10^{-4}
Carbon tetrachloride	5.04×10^{-8}	26.0×10^{-4}
Chloroform	5.38×10^{-8}	17.6×10^{-4}
Carbon disulfide	3.44×10^{-8}	20.10×10^{-5}
Toluene	2.93×10^{-8}	32.71×10^{-5}
Nitrobenzene	8.01×10^{-8}	323.0×10^{-8}
Dioxane	13.13×10^{-8}	182.5×10^{-8}
Amylacetate	31.92×10^{-8}	81.63×10^{-8}
Xylene	40.44×10^{-8}	95.00×10^{-8}
PAC powder	18.10×10^{-8}	6.61×10^{-4}
PAC recrystalized from:		
Carbon tetrachloride	16.93×10^{-8}	1.42×10^{-4}
Carbon disulfide	15.50×10^{-8}	5.59×10^{-4}
Chloroform	13.42×10^{-8}	1.07×10^{-4}
Benzene	11.15×10^{-8}	2.53×10^{-4}

are given in a separate communication.[5] The values for T_{1b} have been calculated with the help of Eqs. (10), (11), and (12). The results of T_{1a} and T_{1b} are given in Table II. The order of T_{1a} in this case is the same as the measured value of T_1 which is represented as $(T_1)_{\text{eff}}$. The value of T_{1b} in class II and class III samples has been found of the order of 10^{-5} sec. In class I samples where the exchange energy has been reduced considerably due to complex formation T_{1b} is of the same order as T_{1a}. The values of K_Z/K_E of these samples is nearly of the order of one and so $(T_1)_{\text{eff}}$ can be written as

$$(T_1)_{\text{eff}} \approx T_{1a} + T_{1b}.$$

In class II and III samples the effective relaxation is by transferring the energy to exchange and the exchange slowly loses that energy to the lattice due to the fact that the exchange reservoir is very large and it can accommodate all the transferred energy without allowing the system to go to higher temperature. In such cases the lattice changes will not affect T_1 very much.

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[5] Krishnaji and B. N. Misra, J. Chem. Phys. 41, 1027 (1964).